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PATENT SPECIFICATION

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(31) Convention Application No. 466 375
(32) Filed 2 May 1974 in
(33) United States of America (US)
(44) Complete Specification published 5 July 1978
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(72) Inventor JAMES VINCENT CRIVELLO



(54) IMPROVEMENTS IN CURABLE EPOXIDE COMPOSITIONS

(71) We, GENERAL ELECTRIC COMPANY, a corporation organized and existing under the laws of the State of New York, United States of America, of 1 River Road, Schenectady 12305, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to curable compositions and in particular epoxy resin compositions which can be cured by exposure to radiant energy.

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PATENTS ACT 1949

SPECIFICATION NO 1516351

The following amendments were allowed under Section 29 on 28 August 1981:

Page 4, line 37, *after catalyst.* insert Lewis Acid means protonic as well as non-protonic acid

THE PATENT OFFICE
6 October 1981

Bas 86007/-

25 These aromatic diazonium salts are capable of releasing, in some, a ~~small amount~~ catalyst which can initiate the rapid polymerization of the epoxy resin. However, even though these one package epoxy resin mixtures can provide fast curing compositions, a stabilizer must be used to minimise cure in the dark during storage of these mixtures. Despite these measures, gellation of the mixture can occur even in the absence of light. In addition, nitrogen is released during UV-cure, which can result in film imperfections. Diazonium salts are generally thermally unstable, rendering the use of such materials hazardous because of the possibility of run-away decomposition. 25

30 Accordingly the present invention provides a curable composition comprising (A) a monoepoxide or an epoxy resin or a mixture thereof polymerizable to a higher molecular weight state, and 30

35 (B) a radiation sensitive aromatic halonium salt in an amount capable of effecting the cure of (A) by release of a Lewis Acid catalyst when exposed to radiant energy. 35

40 A mixture of aromatic halonium salt can be used as a Lewis Acid source if desired. 40

The present invention also provides a method for effecting the cationic polymerization of epoxy material which comprises

(1) forming a mixture of a monoepoxide or an epoxy resin or a mixture thereof and a radiation sensitive aromatic halonium salt capable of effecting the cure

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(54) IMPROVEMENTS IN CURABLE EPOXIDE COMPOSITIONS

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The present invention relates to curable compositions and in particular epoxy resin compositions which can be cured by exposure to radiant energy.

Epoxy resins have generally been employed in a variety of applications requiring high performance materials. Cure of an epoxy resin can generally be achieved by two package systems based on the incorporation into the resin of active amine containing compounds or carboxylic acid anhydrides. These systems require thorough mixing of the ingredients; in addition, cure time can be several hours.

Another catalyst which can be used to cure epoxy resins as "one package" systems is based on the employment of a Lewis Acid catalyst in the form of an amine complex such as boron trifluoride-monoethylamine. The Lewis Acid is released on heating; cure takes place within 1 to 8 hours and can require a temperature of 160°C. and higher. As a result, these one package epoxy compositions cannot be employed to coat heat sensitive devices such as delicate electronic components. Nor can epoxy monomers having low boiling points be used due to the resulting losses to evaporation during cure.

As shown by Schlesinger, U.S. Patent 3,703,296, certain photosensitive aromatic diazonium salts can be employed to cure epoxy resins. When photolyzed, these aromatic diazonium salts are capable of releasing, *in situ*, a Lewis Acid catalyst which can initiate the rapid polymerization of the epoxy resin. However, even though these one package epoxy resin mixtures can provide fast curing compositions, a stabilizer must be used to minimise cure in the dark during storage of these mixtures. Despite these measures, gellation of the mixture can occur even in the absence of light. In addition, nitrogen is released during UV-cure, which can result in film imperfections. Diazonium salts are generally thermally unstable, rendering the use of such materials hazardous because of the possibility of run-away decomposition.

Accordingly the present invention provides a curable composition comprising (A) a monoepoxide or an epoxy resin or a mixture thereof polymerizable to a higher molecular weight state, and (B) a radiation sensitive aromatic halonium salt in an amount capable of effecting the cure of (A) by release of a Lewis Acid catalyst when exposed to radiant energy.

A mixture of aromatic halonium salt can be used as a Lewis Acid source if desired.

The present invention also provides a method for effecting the cationic polymerization of epoxy material which comprises

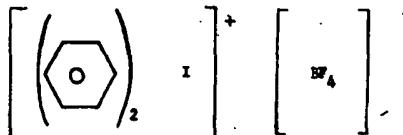
(1) forming a mixture of a monoepoxide or an epoxy resin or a mixture thereof and a radiation sensitive aromatic halonium salt capable of effecting the cure

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of such mixture by the release of a Lewis Acid catalyst when exposed to radiant energy, and

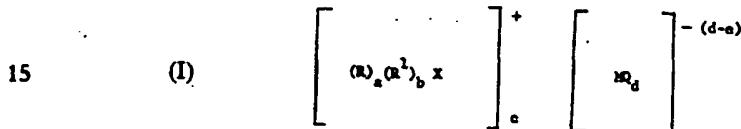
(2) exposing said mixture to radiant energy to effect the cure of the epoxy material.

The present invention is based on the discovery that certain radiation sensitive aromatic halonium salts, such as compounds of the formula,



can be incorporated into epoxy resins to provide one-package radiation curable compositions which do not require a stabilizer to minimise cure at ambient temperatures during the shelf period, and are free of all the aforementioned disadvantages of the above described diazonium salt compositions.

Included among the above shown radiation sensitive aromatic halonium salts which can be used to make the curable compositions of the present invention are compounds of the formula



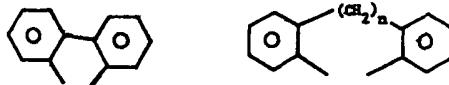
where R is a monovalent aromatic organic radical, R¹ is a divalent aromatic organic radical, X is a halogen radical such as I, Br and Cl, M is a metal or metalloid and Q is a halogen radical such as Cl, F, Br or I, a is 0, and b is 1 or a is 2 and b is 0,

c=3-a

e=valence of M and is an integer equal to 2 to 7 inclusive, and

d is >e and is an integer having a value up to 8.

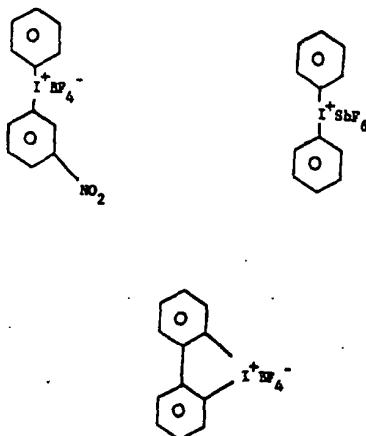
Radicals included by R can be the same or different, aromatic carbocyclic or heterocyclic radical having from 6 to 20 carbon atoms, which can be substituted with from 1 to 4 monovalent radicals selected from, for example, C₁₋₈ alkoxy, C₁₋₈ alkyl, nitro and chloro, R is more particularly, phenyl, chlorophenyl, nitrophenyl, methoxyphenyl or pyridyl. Radicals included by R¹ are divalent radicals such as



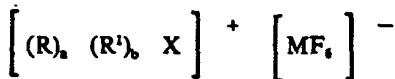
Metal or metalloids included by M of formula I are transition metals such as Sb, Fe, Sn, Bi, Al, Ga, In, Ti, Zr, Sc, V, Cr, Mn, Cs, rare earth elements such as the lanthanides, for example, Cd, Pr and Nd, actinides, such as Th, Pa, U and Np and metalloids such as B, P, and As. Complex anions included by MQ_{d-a} are, for example, BF₄⁻, PF₆⁻, AsF₆⁻, SbF₆⁻, FeCl₆⁻, SnCl₆⁻, SbCl₆⁻, BiCl₆⁻.

Halonium salts included by formula I are, for example,





In one aspect the present invention the salts for use as photoinitiators can be of the formula:



5 where M is P, As or Sb, R is a monovalent aromatic organic radical, R' is a divalent aromatic organic radical, X is a halogen radical, a is 0, 1 or 2, b is 0 or 1, and a + b is equal to 2 or the valence of X. These salts are described and claimed in our Patent Application No. 498/78 (Serial No. 1,516,352).

10 The halonium salts of formula I are well known and can be made by the procedures described by O.A. Ptitsyna, M.E. Pudcova, et al, Dokl. Adad. Nauk, SSSR, 163 383 (1965); Dokl., Chem., 163 671 (1965). F. Marshall Beringer, M. Drexler, E. M. Gindler, etc. J. Am. Chem. Soc., 75 2705 (1953).

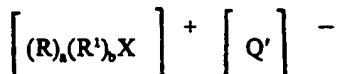
15 The term "epoxy resin" as utilised in the description of the curable compositions of the present invention, includes any monomeric, dimeric or oligomeric or polymeric epoxy material containing one or a plurality of epoxy functional groups. For example, those resins which result from the reaction of bisphenol-A (4,4'-isopropylidenediphenol) and epichlorohydrin, or by the reaction of low molecular weight phenol-formaldehyde resins (Novolak resins) with epichlorohydrin, can be used alone or in combination with an epoxy containing compound as a reactive diluent. Such diluents as phenyl glycidyl ether, 4-vinylcyclohexene dioxide, limoneate dioxide, 1,2-cyclohexene oxide, glycidyl acrylate, glycidyl methacrylate, styrene oxide and allyl glycidyl ether may be added as viscosity modifying agents.

20 In addition, the range of these compounds can be extended to include polymeric materials containing terminal or pendant epoxy groups. Examples of 25 these compounds are vinyl copolymers containing glycidyl acrylate or methacrylate as one of the comonomers. Other classes of epoxy containing polymers amenable to cure using the above catalysts are epoxy-siloxane resins, epoxy-polyurethanes and epoxy-polyesters. Such polymers usually have epoxy functional groups at the ends of their chains. Epoxy-siloxane resins and method for 30 making are more particularly shown by E. P. Plueddemann and G. Fanger, J. Am. Chem. Soc. 81 632-5 (1959). As described in the literature, epoxy resins can also be modified in a number of standard ways such as reactions with amines, 35 carboxylic acids, thiols, phenols, alcohols, etc. as shown in U.S. patents 2,935,488; 3,235,620; 3,369,055; 3,379,653; 3,398,211; 3,403,199; 3,563,850; 3,567,797; and 3,677,995. Further examples of epoxy resins which can be used are shown in the Encyclopedia of Polymer Science and Technology, Vol. 6, 1967, Interscience Publishers, New York, pp 209-271.

40 The curable compositions of the present invention can be made by blending the epoxy resin, which hereinafter will signify epoxy monomer, epoxy prepolymer, oxirane containing organic polymers or a mixture thereof, with an effective amount of the halonium salt. The resulting curable composition which

can be in the form of a varnish having a viscosity of from 1 centipoise to 100,000 centipoises at 25°C can be applied to a variety of substrates by conventional means and cured to the tack-free state within 1 second or less to 10 minutes or more. In other instances, where the epoxy resin is a solid, the curable composition can be a free flowing powder.

Depending upon the compatibility of the halonium salt with the epoxy resin, the halonium salt can be dissolved or dispersed therein along with an organic solvent such as nitromethane and acetonitrile prior to its incorporation. In instances where the epoxy resin is a solid, incorporation can be achieved by dry milling or by melt mixing. *In situ* preparation of the halonium salt by separate or simultaneous incorporation of halonium salt of the formula



where R, R', X, a and b are as previously defined, and Q' is an anion such as Cl⁻, Br⁻, F⁻, I⁻, HSO₄⁻, CH₃SO₄⁻ or NO₃⁻, with the salt of a Lewis Acid of the formula,

15 M'[MQ]

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also has been found to be effective, where [MQ] is as defined above and M' is a metal cation such as Na⁺, K⁺, Li⁺, Ca⁺⁺, Mg⁺⁺, Fe⁺⁺, Ni⁺⁺ and Co⁺⁺, Zn⁺⁺. M' also can be an organic cation such as ammonium group and pyridinium group. Examples of M'[MQ] are NaBF₄, KAsF₆, NaSbF₆, and KPF₆.

20 Experience has shown that the proportion of halonium salt to the epoxy resin can vary widely inasmuch as the salt is substantially inert, unless activated. Effective results can be achieved, for example, if a proportion of from 0.1% to 15% by weight of halonium salt is employed, based on the weight of curable composition. Higher or lower amounts can be used, however, depending upon factors such as the nature of epoxy resin, intensity of radiation and cure time desired.

25 The curable compositions may contain inactive ingredients such as inorganic fillers, dyes, pigments, extenders, viscosity control agents, process aids and UV-screens, in amounts of up to 100 parts filler per 100 of epoxy resin. The curable compositions can be applied to such substrates as metal, rubber, plastic, molded parts or films, paper, wood, glass cloth, concrete and ceramic.

30 Some of the applications in which the curable compositions of the present invention can be used are, for example, protective, decorative and insulating coatings, potting compounds, printing inks, sealants, adhesives, photoresists, wire insulation, textile coatings, laminates, impregnated tapes and printing plates.

35 Cure of the curable composition can be achieved by activating the halonium salt to provide the release of the Lewis Acid catalyst. Activation of the halonium salt can be achieved by heating the composition at a temperature in the range of from 150°C to 250°C. Preferably cure can be achieved by exposing the curable composition to radiant energy such as electron beam or ultraviolet light. Electron beam cure can be effected at an accelerator voltage of from 100 to 1000 KV. Cure of the compositions is preferably achieved by the use of UV irradiation having a wavelength of from 1849 Å to 4000 Å and an intensity of at least 5,000—80,000 microwatts per cm². The lamp systems used to generate such radiation can consist of ultraviolet lamps such as from 1 to 50 discharge lamps, for example, xenon, metallic halide, metallic arc, such as a low, medium or high pressure mercury vapor discharge lamp having an operating pressure of from a few millimeters to 10 atmospheres can be employed. The lamps can include envelopes capable of transmitting light of a wavelength of from about 1849 Å to 4000 Å, and preferably 2400 Å to 4000 Å. The lamp envelope can consist of quartz, such as Spectrocil, and also of Pyrex*. Typical lamps which can be employed for providing ultraviolet radiation are, for example, medium pressure mercury arcs, such as the GE H3T7 arc and the Hanovia* 450 W arc lamp. The cures may be carried out with a combination of various lamps, some or all of which can operate in an inert atmosphere. When using UV lamps, the irradiation flux on the substrate can be at least 0.01 watts per square inch to effect cure of the epoxy resin within 1 to 20 seconds and permit the cure to be carried on continuously as, for example, in the curing of epoxy-coated steel strip to be taken up at a rate of from 100 to 600 feet per minute. The strip can

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be cut to a predetermined width for use as transformer laminates, etc. A combination of heat and light may be used to cure reactive composites. Such a combination of heat and light may serve to reduce the overall cure time.

In order that those skilled in the art will be better able to practice the invention, the following examples are given by way of illustration and not by way of limitation. All parts are by weight.

EXAMPLE 1.

There was added a cooled solution of about 100 ml of acetic anhydride and 70 ml of concentrated sulfuric acid to a suspension of 100 g of potassium iodate in 100 ml of acetic anhydride and 90 ml of benzene. During the addition, the mixture was stirred and maintained below 5°C. When the addition was complete, the reaction mixture was allowed to warm to room temperature and stirred for 48 hours. There was then added 400 ml of distilled water. The aqueous portion of the reaction mixture was extracted three times with diethyl ether and petroleum ether to remove unreacted organic materials. A pale yellow crystalline product formed upon addition of ammonium chloride to the aqueous reaction mixture. There was obtained a 48% yield of diphenyliodonium chloride having a m.p. of 180—185°C. The pure salt had a m.p. of 228—229°C.

A mixture of 20 g of moist, freshly prepared Ag_2O , 10 ml of water and 31.6 g of diphenyliodonium chloride was ground together in a slurry. The wet mixture was filtered and washed with water to produce 360 ml of filtrate. The filtrate was cooled until a substantial amount of the solution had frozen. There was slowly added 25 ml 45—50% HBF_4 , cooled to —15°C. The cold solution was stirred and allowed to warm to room temperature. A white crystalline solid separated and was collected by filtration. There was obtained a 60% yield of diphenyliodonium fluoroborate, m.p. 136°C when the solid was dried overnight *in vacuo* at 60°C.

A curable composition was prepared by dissolving 0.04 part of diphenyliodonium tetrafluoroborate in a small amount of acetonitrile and mixing the resulting solution in 5 parts of 4-vinylcyclohexene dioxide.

The viscosity of the resulting curable composition was found to be initially about 6 centipoises at 25°C. It did not change substantially after several months exposure under normal room lighting.

A portion of the curable compositions was applied as a 0.1 mil film onto a steel strip. The treated steel surface was exposed 15 seconds to the ultraviolet radiation of an H3T7 lamp at a distance of 2 inches. A clear tack-free film was formed which showed no signs of bubbles or other imperfections.

The above treated strip was then immersed in 10C hydrocarbon oil for 48 hours at 120°C to determine its hydrolytic stability in accordance with IFT test ASTM D971—50 Interfacial Tension of Oil Against Water shown on page 322 of the 1970 Annual Book of ASTM Standards, part 17 (November). The initial reading of the oil showed an interfacial tension reading of 38. In order to pass, a reading of at least 30 is required.

EXAMPLE 2.

The procedure of Example 1 was repeated for preparing an aromatic halonium salt using diphenyliodonium chloride. In this preparation, fluoroboric acid was replaced by 25 ml (60%) hexafluorophosphoric acid. There was obtained a 74% yield of diphenyliodonium hexafluorophosphate having a m.p. of 139—141°C.

A curable composition was prepared following the same procedure as Example 1. Comparable results were achieved with respect to its ability to resist change in viscosity over an extended period of time under normal atmospheric conditions. In addition, satisfactory IFT values were also obtained.

EXAMPLE 3.

A curable composition was prepared using a 40:60 solution of 4-vinylcyclohexene dioxide and a novolak-epoxy resin and adding 2% by weight of diphenyliodonium tetrafluoroborate in a small amount of nitromethane.

The curable composition was spread on a glass plate. A mask was then used to cover the treated glass. After irradiation under an H3T7 lamp for 1.5 minutes, the glass was washed with isopropanol. The unexposed portions were washed completely away leaving a negative image of the mask. When the same procedure is repeated using a steel plate as the substrate, the product is useful for the fabrication of printing plates.

EXAMPLES 4-9.

Several curable compositions were prepared in accordance with the procedure shown in Example 1 using 4-vinylcyclohexene dioxide and about 3% by weight of the halonium salt. Various cure times were experienced when the compositions were applied onto a glass substrate and cured at a distance of four inches from a GE H3T7 lamp. The following shows the halonium salt used, its m.p. and the cure times.

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Examples	Halonium Salt		Mp. (°C)	Cure Time* (min.)
	Cation	Anion		
4		BF_4^-	136	0.5
5		PF_6^-	138-141	0.5
6		SbF_6^-	57-58 imp.	0.5
7		BF_4^-	86-100	1
8		BF_4^-	95-100	0.5
9		BF_4^-	133-135	1

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* Time required to cure a 2 mil film containing 3% of the salt at a distance of 4 inches from a G.E. H3T7 lamp.

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EXAMPLE 10.

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To 10 g limonene dioxide were added 0.32 g diphenyliodonium chloride and 0.21 g sodium hexafluoroarsenate. This mixture was heated for 20 minutes at 50°C to achieve metathesis. The salts were allowed to settle and the clear supernatent liquid was drawn off. The sensitized epoxy compound was applied to a steel strip to a thickness of 2 mil and exposed to UV light as described above. Cure took place in 30 seconds. A tough film having good adhesion to the steel plate was obtained.

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EXAMPLE 11.

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Three parts of diphenyliodonium fluoroborate were ground to a fine powder

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5 and tumbled for 30 minutes with 97 parts of Reichhold Epotur* 37-834, a bisphenol A epoxy powder coating resin. The powder blend was then electrostatically sprayed onto 3 in x 6 in steel samples to form a 2 mil coating using a GEMA model 171 spray gun. Subsequently, the samples were heated briefly to 150°C to fuse the powder and then exposed while hot to a GE H3T7 medium pressure mercury arc lamp at a distance of 3 inches. Cured samples were obtained after 30 seconds exposure.

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EXAMPLE 12.

10 Three parts by weight of di-p-tolyl iodonium fluoroborate were added to 97 parts of (3,4-epoxycyclohexyl)-methyl-3,4-epoxycyclohexanecarboxylate. The 10 epoxy resin was then used to impregnate a 1 inch woven glass tape. After winding two turns of the tape onto a 4 in diameter drum, the tape was cured to a rigid glass band by rotating the drum under a GE H3T7 lamp at a distance of 4 inches for 2 minutes. The banding tapes thus prepared can be used as restraining bands in 15 motors and generators.

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The above resin was used to impregnate woven glass cloth. Two 6 in x 6 in 15 squares of the glass cloth were stacked on top of one another and cured for 1 minute on each side. A rigid composite was obtained which is useful for circuit board applications.

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20 A portion of the above mixture was used to impregnate glass roving. The treated glass was then wound onto a 3 in dia. drum to a thickness of about 5 mils. The drum was then rotated beneath a GE H3T7 lamp at a distance of 3 inches for 5 minutes. A measurement of the intensity of the lamp showed that it was approximately 200 watts/sq. inch. When the cured winding was removed from the 25 drum, it was rigid and fully cured. A typical use for such a cured winding is as a spool for electrically conducting wire.

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EXAMPLE 13.

30 A mixture was prepared consisting of 14.5 g (0.25 mole) glycidyl allyl ether, 10 mg. t-butyl-catechol, and 3 drops chloroplatinic acid in octyl alcohol. The reaction 30 mixture was heated to 50°C in a water bath and then 13.0 g of a polydimethyl siloxane resin containing 0.89% by weight Si-H groups was added dropwise by means of a dropping funnel. Immediate exothermic reaction took place with the temperature rising to 65°C. Reaction proceeded smoothly at this temperature giving a clear resin.

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35 Three parts by weight of 4-methoxydiphenyliodonium fluoroborate dissolved in a small amount of methylene chloride was added to 97 parts of the above 35 silicone epoxy resin. A 2 mil film of the sensitized resin was drawn on a steel plate and then exposed to UV light from a GE H3T7 lamp at a distance of six inches. The film was tack-free within 10-15 seconds. A small amount of silica was added to the sensitized resin to produce a thixotropic mixture and the resin cured as 40 described previously. A tough, rubbery coating resulted.

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EXAMPLE 14.

45 A solution of 3 parts of 4-methoxydiphenyliodonium fluoroborate dissolved in 20 parts of 4-vinyl-cyclohexene dioxide was added to 80 parts of a glycidyl methacrylate-methyl methacrylate copolymer having a molecular weight of 8,500 and a glycidyl acrylate content of 5% by weight. This mixture was mixed by rolling it in a 45 glass bottle on a ball mill overnight. The viscous solution was knife coated onto a glass plate to give a 2 mil film which when irradiated at a distance of six inches from a FE H3T7 lamp, gave a clear hard coating in 10 seconds. The film was highly crosslinked and insoluble in all common solvents.

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55 Three parts of diphenyliodonium hexafluoroarsenate were dissolved in 6.7 parts of methylene chloride and the solution added to 97 parts glycidyl acrylate. A 3 part aliquot of this highly fluid mixture was placed in an aluminum cup and then exposed to the ultraviolet irradiation of a H3T7 lamp using a water filter. The cure time was 15 seconds. Subsequent analysis showed that the conversion to polymer was greater than 95%. A hard glossy resin was obtained.

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EXAMPLE 15.

A blend was prepared using equal parts of 4-vinyl-cyclohexene dioxide and

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(3,4-epoxycyclohexyl)methyl-3,4-epoxycyclohexanecarboxylate. To this blend were added four parts of diphenyliodonium fluoroborate. An aliquot of the above sensitized resin was spread onto a sheet of Lexan polycarbonate using a draw-down blade to give a 0.5 mil film. The film was cured as described in Example 3 for 20 seconds giving a clear hard coating which provides mar and solvent resistance for the substrate polymer.

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A mixture of 50 parts bisphenol-A-diglycidyl ether and 50 parts (3,4-epoxycyclohexyl)methyl-3,4-epoxycyclohexanecarboxylate was stirred until homogeneous and then 3 parts by weight diphenyliodonium hexafluoroantimonate in a small amount of methylene chloride was added and the solution thoroughly mixed. A portion of the above sensitized solution was coated onto a steel plate using a 0.2 mil drawbar. The plate was then irradiated for 10 seconds using a GE H3T7 mercury arc lamp at a distance of six inches. The completely cured, hard, glossy film had excellent adhesion to the steel and could not be removed by rubbing it with acetone.

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EXAMPLE 17.

A blend of epoxy resins consisting of 50 parts 4-vinylcyclohexane dioxide, 40 parts of a novolak-epoxy resin having an epoxy equivalent weight of 172-178 and 10 parts n-decylglycidyl ether were thoroughly mixed together. A 100 part aliquot was taken and 1 part diphenyliodonium hexafluorophosphate was added and the resulting mixture stirred until the catalyst had dissolved. When the above mixture was coated onto a 3 in x 6 in panel and then exposed to a 450 watt medium pressure mercury arc lamp at a distance of 3 inches, a glossy, dry coating was obtained in 3 seconds. The coating withstood attack by hot boiling water for four hours and could not be removed by rubbing with acetone.

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EXAMPLE 18.

A blend of epoxy resins consisting of 50 parts 4-vinylcyclohexane dioxide, 40 parts of a novolak-epoxy resin having an epoxy equivalent weight of 172-178 and 10 parts n-decylglycidyl ether were thoroughly mixed together. A 100 part aliquot was taken and 1 part diphenyliodonium hexafluorophosphate was added and the resulting mixture stirred until the catalyst had dissolved. When the above mixture was coated onto a 3 in x 6 in panel and then exposed to a 450 watt medium pressure mercury arc lamp at a distance of 3 inches, a glossy, dry coating was obtained in 3 seconds. The coating withstood attack by hot boiling water for four hours and could not be removed by rubbing with acetone.

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EXAMPLE 19.

There was added 1 g of di-p-tolylodonium fluoroborate to a mixture of 40 g limonene dioxide and 10 g of a epoxy Novolak (phenolformaldehyde) resin having an epoxy equivalent weight of 210-240. The mixture was stirred at 50°C for 1 hour to produce a homogeneous solution of the components. When the mixture was coated onto a glass plate using a 0.5 mil drawbar, a hard, adherent, cured film was produced by irradiating the sample for 5 seconds at a distance of 3 inches from a GE H3T7 lamp which has an intensity of 200 watts/sq. inch.

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There was added 0.2 part p-methoxydiphenyliodonium fluoroborate in 2 parts 4-vinylcyclohexene dioxide to 10 parts of epoxidized butadiene. After mixing, a 1 mil coating of the resulting mixture was applied onto a 1/16 inch thick glass plate. Another plate of glass was placed on top of the first and this assembly exposed to a GE H3T7 medium pressure mercury arc lamp having an intensity of 200 watts/sq. in. at a distance of 3 inches. The total time of exposure was 1 minutes. The glass plates were permanently bonded together and the glass laminate could be used as a shatterproof windshield for automobiles.

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EXAMPLE 20.

There was added 0.2 part p-methoxydiphenyliodonium fluoroborate in 2 parts 4-vinylcyclohexene dioxide to 10 parts of epoxidized butadiene. After mixing, a 1 mil coating of the resulting mixture was applied onto a 1/16 inch thick glass plate. Another plate of glass was placed on top of the first and this assembly exposed to a GE H3T7 medium pressure mercury arc lamp having an intensity of 200 watts/sq. in. at a distance of 3 inches. The total time of exposure was 1 minutes. The glass plates were permanently bonded together and the glass laminate could be used as a shatterproof windshield for automobiles.

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Although the above examples are limited to only a few of the very many curable compositions and uses thereof which are included within the scope of the present invention, it should be understood that the present invention is intended to cover a much broader class of curable compositions and uses thereof. Those

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skilled in the art would also know that the curable compositions also cover the use of halonium polymers containing halonium functionality as part of the polymer backbone or in the pendant position.

WHAT WE CLAIM IS:—

5 1. A curable composition comprising

(A) a monoepoxide, an epoxy resin or a mixture thereof polymerizable to a higher
10 molecular weight state, and

(B) a radiation sensitive aromatic halonium salt in an amount capable of effecting
15 the cure of (A) by release of a Lewis Acid catalyst when exposed to radiant
energy.

2. A composition in accordance with claim 1, where the aromatic halonium
salt is a diphenliodonium salt.

3. A composition in accordance with claim 2, where the complex anion of the
diphenliodonium salt is a tetrafluoroborate.

4. A composition in accordance with claim 2, where aromatic iodonium salt is
diphenliodonium hexafluorophosphate.

5. A composition in accordance with claim 2, where the complex anion of the
diphenliodonium salt is a hexafluoroantimonate.

20 6. A composition in accordance with claim 2, where the complex anion of the
diphenliodonium salt is a hexafluoroarsonate.

7. A composition in accordance with any one of Claims 1—6 where the
aromatic halonium salt is prepared *in situ*.

8. A composition in accordance with any one of Claims 1—7 where a mixture
25 of aromatic halonium salts are employed as the Lewis Acid source.

9. A composition in accordance with any one of Claims 1 to 8 in the form of a
fluid at room temperature.

10. A composition in accordance with any one of Claims 1 to 8 in the form of a
free-flowing powder.

30 11. A printing ink of/or containing a composition in accordance with any one
of Claims 1—10.

12. A method for effecting the cationic polymerization of epoxy material
which comprises

(1) forming a mixture of a monoepoxide, an epoxy resin or a mixture thereof and a
35 radiation sensitive aromatic halonium salt in an amount capable of effecting
the cure of such mixture by the release of a Lewis Acid catalyst when exposed
to radiant energy, and

(2) exposing said mixture to radiant energy to effect the cure of the epoxy resin.

40 13. A method in accordance with Claim 12, where the cure is effected with
ultraviolet light.

14. A method in accordance with Claim 12, where the cure is effected with
electron beam.

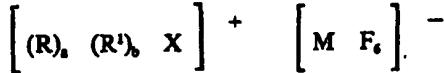
45 15. A method in accordance with any of Claims 12—14 where the cured epoxy
resin is subsequently heat treated.

16. A method in accordance with any one of Claims 12 to 15, where the
mixture is applied to a substrate prior to cure.

50 17. A method in accordance with Claim 16, where the mixture is applied to
the substrate by use of an organic solvent.

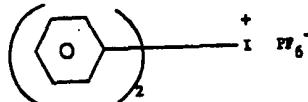
18. A method in accordance with Claim 16 or 17, where a mask is employed to
generate a photo image.

19. A method as claimed in any one of claims 12 to 18 wherein the salt has the
formula

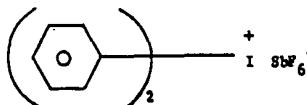


where M is P, As or Sb, R is a monovalent aromatic organic radical, R¹ is a divalent aromatic organic radical, X is a halogen radical, α is 0, and b is 1 or α is 2 and b is 0.

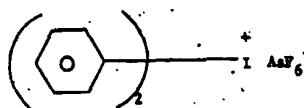
20. A method as claimed in Claim 19 where M is P and X is I.
21. A method as claimed in Claim 19 wherein the salt has the formula:



22. A method as claimed in Claim 19 wherein the salt has the formula:



23. A method as claimed in Claim 19 wherein the salt has the formula:



5 24. A curable composition comprising:

(A) a monoepoxide, an epoxy resin or a mixture thereof polymerizable to a higher molecular weight state, and
 (B) a radiation sensitive salt having the formula



10 where M is P, As or Sb, R is a monovalent aromatic organic radical, R¹ is a divalent aromatic organic radical, X is a halogen radical, a is 0 and b is 1, or a is 2 and b is 0.

10

25. A composition as claimed in claim 24 where M is P and X is I.

26. A composition as claimed in claim 24 where the salt has the formula:



15

27. A composition as claimed in claim 24 where the salt has the formula:



28. A composition as claimed in claim 24 wherein the salt has the formula:



20 29. A curable composition as claimed in claim 1 substantially as hereinbefore described in any one of the examples.

20

30. A composition as claimed in any one of claims 1 to 10 and 24 to 29 when cured.

25 31. A method of effecting the cationic polymerization of epoxy resin as claimed in claim 12 substantially as hereinbefore described in any one of the examples.

25

32. A polymer when produced by a method as claimed in any one of claims 12 to 23 and 31. 5

33. A protective, decorative or insulating coating, a potting compound, a printing ink, a sealant, an adhesive, a photoresist, a wire insulation, a textile coating, a laminate, an impregnated tape or a printing plate of/or containing a composition as claimed in any one of claims 1 to 10, 24 to 30, or a polymer as claimed in claim 32. 5

34. An article of manufacture comprising a substrate treated with the composition of any one of claims 1 to 10 or 24-30. 10

35. A fibre glass composite comprising a substrate in accordance with claim 34. 10

PAUL M. TURNER,
Agent for the Applicants.

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